

A REVIEW OF TIN OXIDE-BASED CATALYTIC SYSTEMS:
PREPARATION, CHARACTERIZATION AND CATALYTIC BEHAVIOR

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SUMMARY

This paper reviews the important aspects of the preparation, characterization and catalytic behavior of tin oxide-based catalytic systems including doped tin oxide, mixed oxides which contain tin oxide, Pt supported on tin oxide and Pt/Sn supported on alumina. These systems have a broad range of applications and are continually increasing in importance. However, due to their complex nature, much remains to be understood concerning how they function catalytically.

INTRODUCTION

It is only recently that the importance of tin oxide-based catalytic systems has begun to be recognized. These catalysts occur in many forms and are used in a wide range of applications from electrocatalysis to gas-phase reactions. Other than the fact that they all contain tin oxide, a common attribute is their complexity with regard to composition, geometrical structure, electronic structure, redox behavior and catalytic properties. The purpose of this review is to briefly describe some important aspects relating to these catalytic systems and to provide more detailed sources concerning these discussions.

I. OXIDATION OF METALLIC TIN

In these systems it is possible for tin to be present in various forms including metallic and/or as either stable oxide SnO or SnO_2 , alloyed with another metal such as Pt (PtSn or Pt_3Sn), and others. Studying the oxidation of metallic tin using various characterization techniques often allows for the identification of the different species present in more complex environments. Different techniques including Auger electron spectroscopy (AES) (1-4), ultra-violet photoemission spectroscopy (UPS) (5), electron spectroscopy for chemical analysis (ESCA) (3,4,6), electron energy loss spectroscopy (ELS) (1,2,7), low energy electron diffraction (LEED) (2) and thermal gravimetry (8) have been used to examine the oxidation of metallic tin as a function of oxygen exposure (1,2,4,7) and temperature (2,8).

Much information which is useful in characterizing the Pt/SnO_x system is contained in these studies. Both of the two stable oxides SnO and SnO_2 are always present during the oxidation process, and it is very difficult to distinguish

between them using ESCA or AES particularly quantitatively since most of their spectral features are essentially identical. However, it has been demonstrated that valence-band ESCA (6) and ELS (1,2) are capable of distinguishing between SnO and SnO₂. The relative amounts of each oxide present vary considerably with the conditions of oxidation. For heavily oxidized samples, an SnO₂ layer lies beneath an oxygen-depleted or SnO-like layer. Another important point is that the work function of the surface does not change as it becomes oxidized. This fact combined with the fact that SnO and SnO₂ have the same ESCA 3d binding energies provides an excellent means of referencing all spectral features. This eliminates the need to use questionable references such as the C 1s peak (due to contamination) or to make tedious work function corrections.

It is important to understand that both ESCA and AES examine a fairly large number of atomic layers in the surface region and are not as surface sensitive as they are often considered to be. One of the most surface-sensitive techniques is ion scattering spectroscopy (ISS) which is essentially outermost layer sensitive. A recent ISS study carried out in the author's laboratory has demonstrated that a room temperature, saturation exposure to oxygen results in penetration of the oxygen beneath the outermost layer of tin atoms. Scanning Auger microscopy (SAM) shows that this penetration occurs at planar lattice sites and not at grain boundaries.

II. CHARACTERIZATION AND PROPERTIES OF TIN OXIDE

Tin oxide is an n-type, wide-gap, semiconducting oxide material which is transparent to visible light. Consequently, it is important as an electrode material (9-14), in solar cell applications (15,16), as a sensor material (17-19) and as a transparent conductor in electronic displays (20,21). The chemical activity of tin oxide and particularly its redox properties make tin oxide an important catalytic material in both a pure and mixed oxide form for gas-phase reactions (22-37) and for electrocatalytic or photoelectrocatalytic reactions (38-46). Although tin oxide functions as an oxidative catalyst in most of these studies, it is interesting that it can also function in a reductive manner.

Tin oxide is an exceedingly complex material with regard to geometrical structure and composition. Both stable oxides are always present, and each can be in several structural forms including defect-laden structures. Hydrogen is always present in tin oxide in varying amounts and binding states (47), and large quantities of contaminants including C, Ca, K, Na, S and Cl are usually present (48). Furthermore, nearly any treatment of a tin oxide surface alters it in some manner. Based on a large number of characterization studies, it is not possible to understand the complex properties of tin oxide by considering it to be a relatively simple material such as SnO₂. Therefore, it is necessary to develop and utilize characterization techniques which are sensitive to all of the various complex aspects of tin oxide surfaces. Furthermore, the use of multiple techniques on a particular tin oxide surface provides the most complete information about that surface.

AES and secondary ion mass spectrometry (SIMS) are both useful for observing contaminants at tin oxide surfaces. ESCA is often less useful since it is not as surface sensitive as either AES or SIMS or as sensitive to trace amounts. A typical AES spectrum taken from a contaminant antimony-doped tin oxide surface is

shown in figure 1 (48). Antimony is often added to tin oxide because it lowers its electrical resistivity by several orders of magnitude or can improve its catalytic properties. The contamination was present in the various chemicals and apparatus used to prepare the tin oxide film. By using extremely pure chemicals

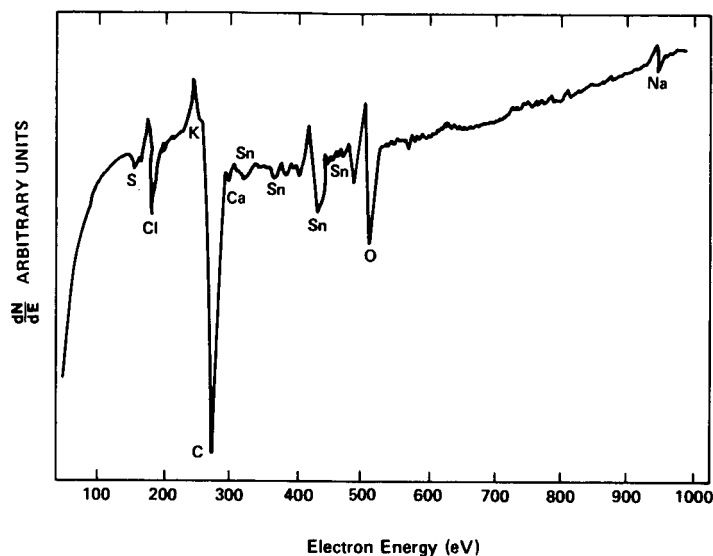


Figure 1. Typical AES spectrum (low energy resolution) taken from a contaminated antimony-doped tin oxide surface. The K and Ca peaks are masked by the large C peak (ref. 48).*

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and meticulously cleaning all apparatus, it is possible to prepare tin oxide surfaces which are only slightly contaminated with a small amount of C. It has been found that the Ca contamination is due to allowing the solutions to sit in glassware, and the amount present depends upon the length of time they remain in the glassware. The oxygen-to-tin ratio in figure 1 is larger than that of an SnO_2 -like surface indicating that excess oxygen is present probably as hydroxyl groups, water of hydration or bound to other impurities.

AES is insensitive toward some elements. Examples are Sb and H. Small amounts of Sb are masked by larger Sn features, and H has no distinct AES peaks since it has no core-level electrons. However, both can readily be observed using SIMS. Sb appears in the SIMS negative-ion spectrum as SbO^- (153 and 155 amu) and SbO_2^- (49). Hydrogen influences many m/e peaks in the SIMS positive-ion spectrum (50). Apparently the m/e = 121 peak gives the least ambiguous measure of the amount of H present. It is assigned as 120 SnH^+ and is least affected by scrambling with other tin isotope species. However, it is very difficult to quantify SIMS results since cross sections can vary by orders of magnitude and are not well understood.

Both AES and SIMS are destructive techniques. SIMS alters the surface composition by ion sputtering, and AES alters the surface composition by electron stimulated desorption (ESD). Thus, it is necessary to use very low primary beam doses and to take repeated spectra to be certain that beam damage has not altered the information. Although ESD is a predominant type of damage phenomena in AES, it is now used as a very powerful surface analytical technique (51). Mass analysis, energy analysis, angular distributions and desorption thresholds of the emitted

ions yield important information about binding states of the adsorbed species. Particularly important is the fact the ESD provides an excellent method for studying surface hydrogen since it is a mass spectrometric technique. This point is illustrated in figure 2 (51,52). Figure 2(A) shows the H^+ and O^+ ESD signals

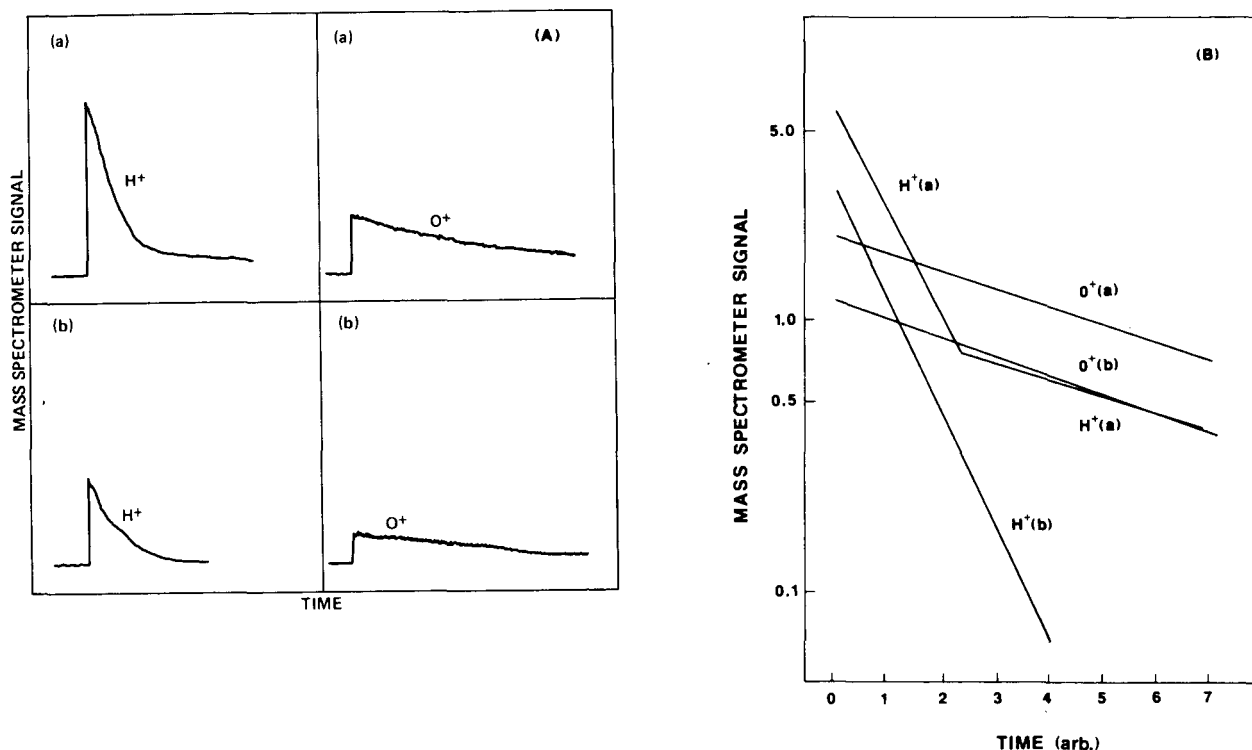


Figure 2. (A) H^+ and O^+ signals as a function of time from a polycrystalline tin oxide surface which had been a: exposed to a 10 M NaOH solution for 30 minutes at 90°C and b: exposed only to atmospheric humidity. The heights are arbitrary but scaled relatively to each other. Both treatments resulted in surface hydroxylation but to different extents. (B) Plots of $\ln i^+$ vs time for the spectra shown in (A). Two adsorbed states of hydrogen appear for the caustic-treated sample whereas only one appears for the air-exposed sample.

as a function of time from (a) a polycrystalline tin oxide surface which had been exposed to a 10 M NaOH solution for 30 minutes at 90°C and (b) a polycrystalline tin oxide surface exposed only to atmospheric humidity. Both surfaces are hydroxylated, but the hydroxyl group concentration is considerably greater for the caustic-treated surface. Plots of $\ln i^+$ versus time of the spectra shown in figure 2(A) show that two adsorbed states of hydrogen are present on the caustic-treated surface whereas only one appears for the air-exposed sample. The presence of multiple binding states of H on a caustic-treated sample has been verified recently using energy analysis of the desorbing H^+ ions (ESDIED).

ELS is another technique which is extremely useful in characterizing tin oxide surfaces particularly when combined with a valence-band photoemission technique. The difficulty in using ELS lies in interpreting the complex spectra. However, interpretation of the spectra as a mixture of surface plasmons, bulk plasmons and optically allowed interband and intraband transitions yields a satis-

factory understanding of the spectral features (52,53). In order to make an appropriate interpretation, electronic-structure information is required from filled-energy level experiments such as ESCA or VPS, unfilled-energy level experiments such as inverse photoemission spectroscopy (IPS), Bremsstrahlung spectroscopy or constant initial state UPS, and theory (54-59). After construction of the complete electronic structural diagram from high lying core levels to about 50 eV above the Fermi level for both SnO and SnO₂, it is possible to assign ELS features as plasmons and electronic transitions using dipole selection rules. A typical set of ELS spectra taken from a vacuum-annealed tin oxide surface are shown in figure 3. The spectra shown were taken using electron beam energies from 200 to

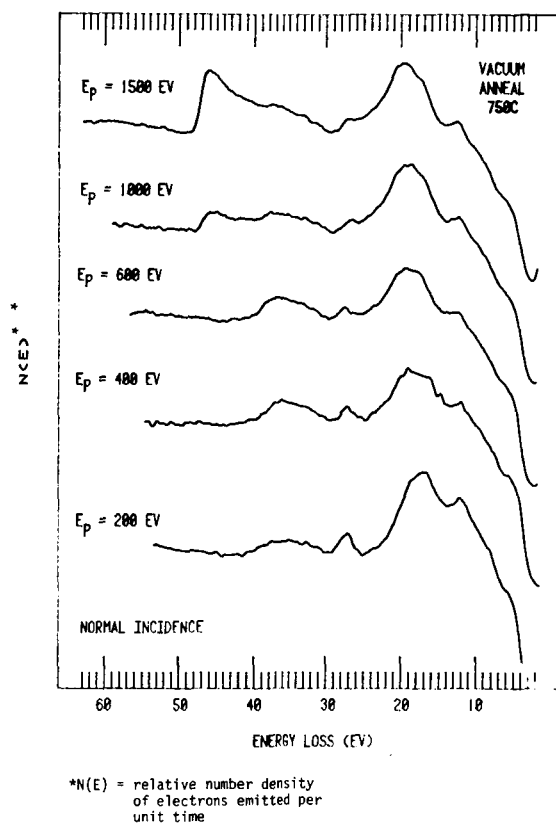


Figure 3. Variation in the $N(E)$ ELS spectrum with primary beam energy E_p . The sets of spectra are essentially a depth profile of the annealed material. Assignment of the features is given in ref. 53.

1500 eV. Increasing the primary beam energy results in a less surface sensitive spectrum. The 1500 eV spectrum is characteristic of bulk SnO₂ while the 200 eV spectrum is more SnO like. The small peak at 27 eV is only dipole allowed for SnO. Note that its contribution decreases as the primary beam energy increases.

Valence-band features are also sensitive to SnO, SnO₂ defects and hydroxyl groups. This is illustrated in figures 4 and 5. Figure 4(A) shows the valence band after annealing the tin oxide at 600°C. This spectrum is characteristic of

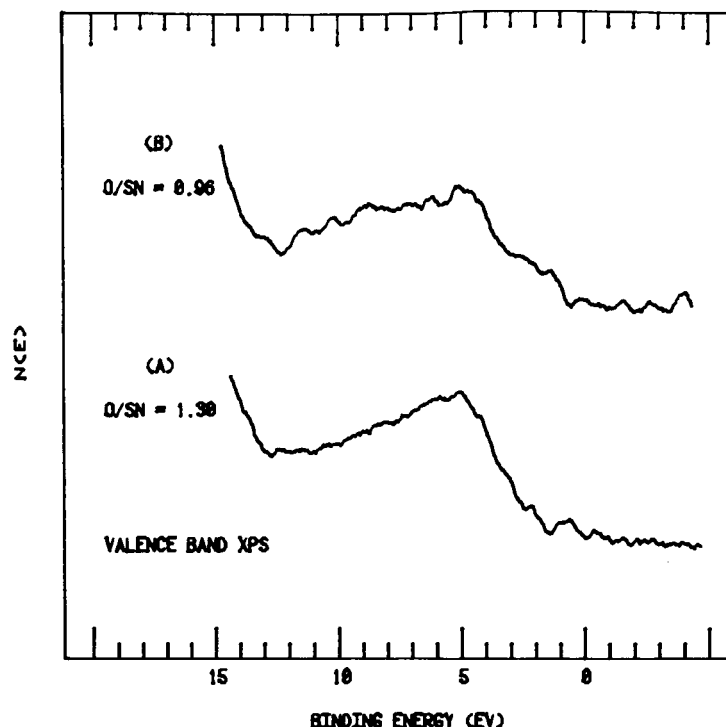


Figure 4. Valence-band ESCA spectra taken after (A) annealing at 600°C and (B) after bombardment with 2 keV argon ions.

bulk SnO_2 . Spectrum (B) was taken after sputtering the surface with 2 keV argon ions. A broad defect structure is observed in the bandgap and SnO features are apparent below the Fermi level. Annealing in oxygen converts the valence-band spectrum back to that shown in (A), and corresponding changes appear in the ELS spectra. Figure 5 shows the valence-band spectrum of a hydroxylated tin oxide surface in (A). The large feature at about 10 eV is due to emission from hydroxyl groups. Annealing at 500°C greatly reduces the size of this peak (spectrum (B)), and annealing at 600°C completely eliminates it leaving an SnO_2 spectrum (spectrum (C)). This behavior is consistent with the bulk dehydration study of Giesekke et al. (47). A distinct peak due to hydroxyl groups also appears in ELS spectra (60).

III. PREPARATION AND CHARACTERIZATION OF PLATINIZED TIN OXIDE

Due to the importance of platinized tin oxide and the unique properties of tin oxide, numerous methods of producing these surfaces have been developed. Katayama (61,62) has discussed the preparation and ESCA characterization of platinized tin oxide electrodes. In these studies ethanol solutions containing SnCl_4 , SbCl_3 and H_2PtCl_6 were sprayed onto glass substrates held at 550°C. It is also possible to form a tin oxide layer first by hydrolysis of a tin chloride solution in hydrochloric acid and then deposit the Pt (63). The Pt can be deposited using

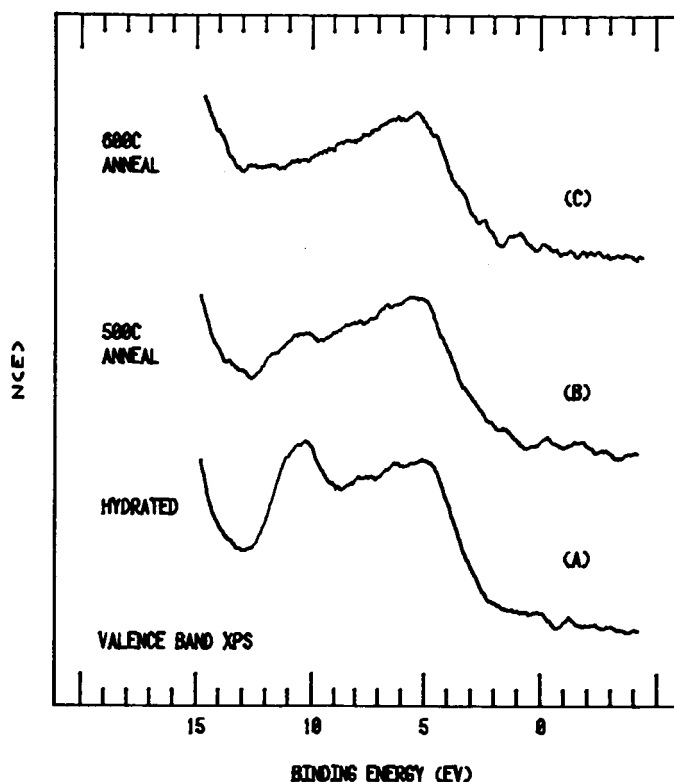


Figure 5. Valence-band XPS spectra taken from a tin oxide surface after (A) hydroxylation by exposure to atmospheric humidity, (B) annealing at 500°C in vacuum for 45 minutes and (C) annealing in vacuum at 600°C for 30 minutes.

one of several different methods including (1) impregnation (chemisorption of a Pt-containing species), (2) an electrochemical deposition, (3) spray hydrolysis, (4) deposition from a molten salt mixture or (5) thermal decomposition of a platinum-containing organic compound such as platinum acetyl acetonate. Watanabe et al. (64) have discussed the pretreatment and chemisorption variables which yield Pt loadings of 0.2 to 1 $\mu\text{g}/\text{cm}^2$ and high dispersions (> 0.9). As described in an earlier study (63), an alkaline pretreatment consisting of immersing the tin oxide in 10M NaOH at 90°C was found to be important. A platinizing solution consisting of 1000 ppm Pt (IV), 0.135M NaH_2PO_4 and 0.5M NaCl was found to be most effective in the platinization process. Rutherford back-scattering was used to determine the total amount of Pt present (65), and electrochemical reduction of H^+ was used to determine the concentration of surface Pt atoms. Impregnation of Pt and Sn onto an alumina surface from an acetone solution containing SnCl_4 and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ has been used by Davis (66) and Hoflund et al. (67).

There are two different ways of depositing Pt electrochemically. The first is to simply use cathodic plating conditions from a Pt salt-containing electrolyte

(63). The second is to select an appropriate chemisorption reaction and to influence this reaction using anodic potentials. This process has been examined thoroughly for the case of electrochemisorption of hexahydroxyplatinate onto tin oxide over a potential range of 0.0 to 1.0V versus SCE (68). Figure 6 shows the

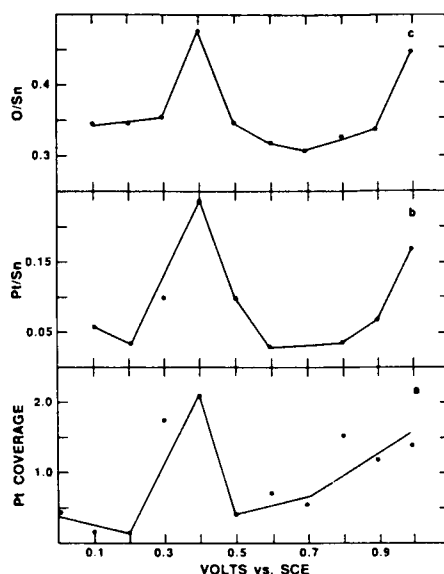


Figure 6. Amount of Pt deposited from a solution containing 0.01 M KOH, 2.56×10^{-3} M $\text{Na}_2\text{Pt}(\text{OH})_6$, and 1.0M NaClO_4 . Curve a shows the results of the electro-chemical determination. Curve b shows the results of an ESCA determination, and curve c shows the O-to-Sn ratio determined from corrected O 1s and Sn 3d peak area.

amount of Pt deposited as a function of potential. A large maximum occurs at a potential of 0.4V versus SCE which is believed to be due to the formation of active surface intermediates. An ESCA analysis of the deposited Pt also shows that its chemical state varies in a similar way as the amount. This dependence is shown in figure 7 which is a plot of the ESCA Pt 4f binding energy versus potential. Larger values suggest a more oxidized form of the Pt, and again a maximum is observed at about 0.4 eV.

The chemical state of the Pt in Pt/Sn is an important topic which has been considered in several studies (61-63,67-77). Most of these studies rely upon the use of ESCA or Mössbauer for chemical state determination. An ESCA study by Cox et al. (69) of Pt chemisorbed on polycrystalline tin oxide shows that it is possible to alter the chemical state of Pt by various oxidative and reductive treatments. This is illustrated in figure 8 for a lightly loaded sample. Heating the as-prepared sample (A) at 600°C in 11 Torr of O_2 for 30 minutes produces a mixture of PtO and PtO_2 (B) while annealing in hydrogen (C) or vacuum (D) reduces the Pt to mostly metallic form. Related results from a thin film of Pt/SnO_x deposited on alumina are shown in figure 9 (67). In this case the samples were heated in air at 450°C (a) and under 1 atm of H_2 at 500°C (b). Similar chemical state changes are observed in this figure. Furthermore, it appears that exposure to air does not oxidize Pt to metallic form. Since the Pt/SnO_x system is stable at 800°C in vacuum, the bonds between the Pt and substrate must be strong chemical

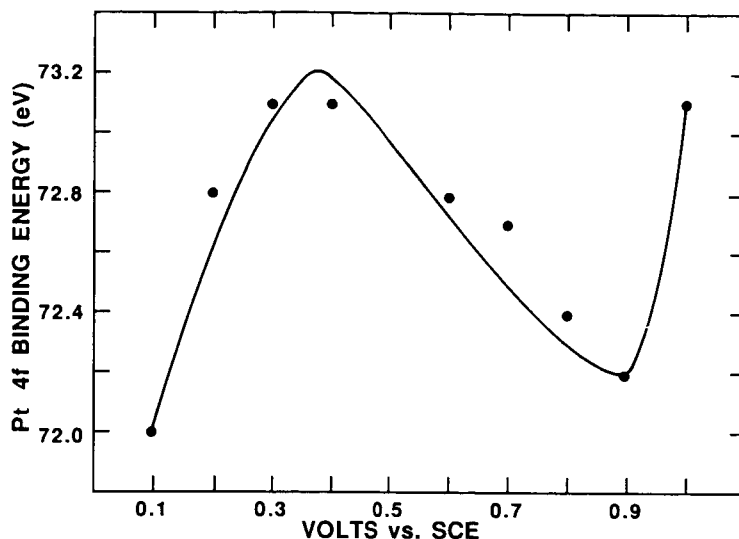


Figure 7. Average binding energies of the low binding energy ESCA Pt 4f peaks as a function of deposition potential.

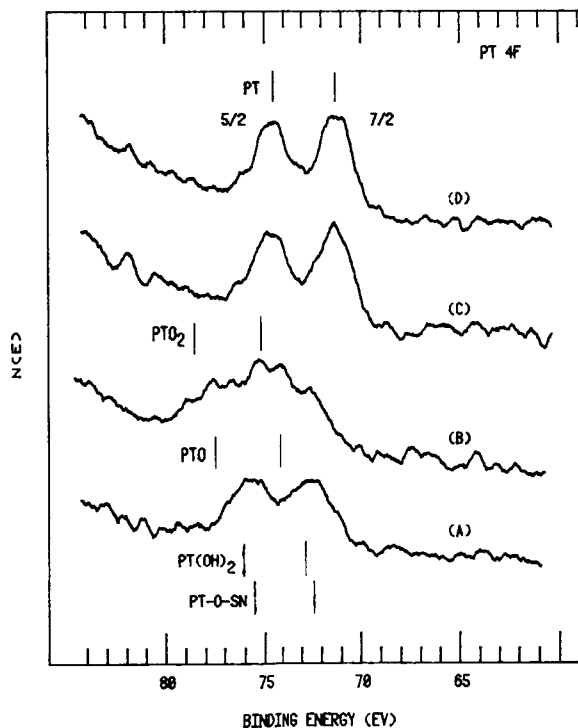


Figure 8. Pt 4f XPS spectra of a sample prepared by platinum chemisorption obtained (A) immediately after pumpdown, (B) after high-temperature oxidation, (C) after high-temperature reduction, and (D) after a high-temperature anneal in vacuo.

bonds. These ESCA studies all suggest that Pt-O-Sn bonds anchor the Pt to the substrate. They also suggest that a crude measure of the dispersion can be obtained from the binding energy of the metallic Pt 4f peaks (see figure 9b). In

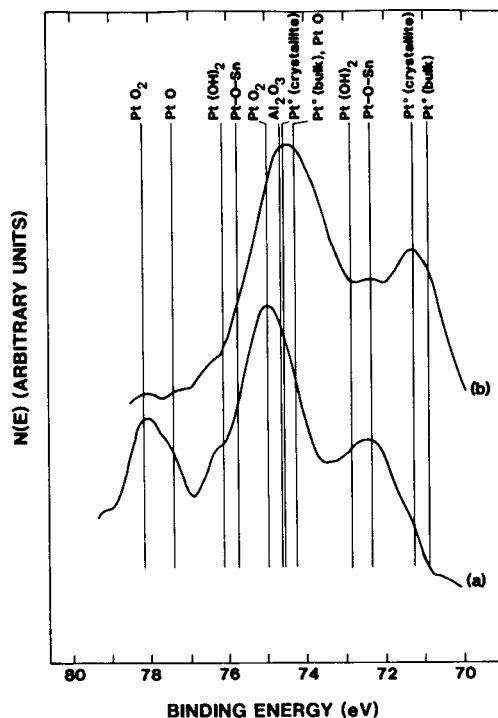


Figure 9. High resolution ESCA spectra of the Pt 4f peaks of an oxidized sample (curve a) and a reduced sample (curve b).

these studies small amounts of Cl were present on the surface which may have facilitated the changes between oxidation states. Similar experiments on Cl-free surfaces have not yet been performed.

Much controversy still exists in the literature concerning the nature of the Pt/Sn interaction. Several studies (70-72) suggest that a Pt/Sn alloy is present. However, two facts suggest that this may not be the case. The first is that studies of Pt/Sn alloys (78-80) generally show that they are poor catalysts and that their performance deteriorates with increasing surface tin concentration. The second is that other studies show that metallic tin is not present even after reduction (73-77). Clearly, more effort will be required to understand the actual situation and resolve the various controversies. However, studies of the two stable Pt/Sn alloys PtSn and Pt₃Sn (81-85) should prove useful in understanding Pt/Sn catalytic systems.

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